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Fibrillar Electronically Conductive Polymers Show Enhanced Rates  
of Charge-Transport

by

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<p>Many electronically conductive polymers (1) can be reversibly switched between electronically insulating and electronically conducting states (2). For polypyrrole, this redox switching reaction can be written as</p> $(Py)_x + nBF_4^- \rightleftharpoons (Py)_x^{+} BF_4^- - (Py)_{x-n}^{+} + ne^-$ <p>where Py and <math>Py_x^{+}</math> are reduced and oxidized monomer units in the polypyrrole film and <math>BF_4^-</math> is a charge balancing counter-ion, initially present in a contacting solution phase. Equation 1 shows that ions must be incorporated into, or expelled from, the polymer phase during the redox switching reaction. In many cases, the rate of this reaction is controlled by ion-transport in the polymer phase (3,4).</p> <p>The switching reaction plays an integral role in nearly all of the proposed applications of electronically conductive polymers (5-7). In most cases, significant benefit would accrue if the rate of this reaction could be accelerated. (Continued on reverse)</p>					
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The above discussion suggests that one approach for enhancing the rate of the switching reaction would be to enhance the rate of charge-transport in the polymer phase.

We have recently described a procedure for controlling the supermolecular structures of electronically conductive polymers (8). This procedure yields polymers with fibrillar supermolecular structures. We have shown that polypyrrole films which have this fibrillar supermolecular structure support higher rates of reductive charge-transport than conventional polypyrrole films. We report preliminary results of these investigation in this communication.

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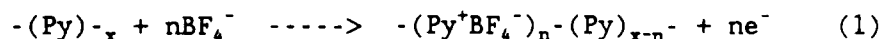
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## INTRODUCTION

Many electronically conductive polymers [1] can be reversibly switched between electronically insulating and electronically conducting states [2]. For polypyrrole, this redox switching reaction can be written as



where Py and  $\text{Py}^+$  are reduced and oxidized monomer units in the polypyrrole film, and  $\text{BF}_4^-$  is a charge balancing counter-ion, initially present in a contacting solution phase. Equation 1 shows that ions must be incorporated into, or expelled from, the polymer phase during the redox switching reaction. In many cases, the rate of this reaction is controlled by ion-transport in the polymer phase [3,4].

The switching reaction plays an integral role in nearly all of the proposed applications of electronically conductive polymers [5-7]. In most cases, significant benefit would accrue if the rate of this reaction could be accelerated. The above discussion suggests that one approach for enhancing the rate of the switching reaction would be to enhance the rate of charge-transport in the polymer phase.

We have recently described a procedure for controlling the supermolecular structures of electronically conductive polymers [8]. This procedure yields polymers with fibrillar supermolecular structures. We have shown that polypyrrole films which have this fibrillar supermolecular structure support higher rates of reductive charge-transport than conventional polypyrrole films. We report preliminary results of these investigations in this communication.

## EXPERIMENTAL

All reagents were purified as described previously [9]. The instrumentation used has also been previously described [9]. Results from two different types of polypyrrole will be discussed here. These are - ordinary polypyrrole which was electrochemically synthesized at a conventional Pt disk electrode [9], and fibrillar polypyrrole which was synthesized within the pores of a microporous host membrane [8]. Throughout this paper these materials are referred to as "conventional polypyrrole" and "fibrillar polypyrrole."

Preparation of Fibrillar Polypyrrole. Fibrillar polypyrrole was prepared by electrochemically synthesizing the polymer within the pores of commercially available Anopore  $\text{Al}_2\text{O}_3$  filtration membranes [10]. These membranes contain linear, cylindrical,  $0.2\text{ }\mu\text{m}$ -diameter pores. The porosity is ca. 65 %; the membranes are ca.  $50\text{ }\mu\text{m}$  thick.

In order to synthesize polypyrrole in the pores, one surface of the Anopore membrane must be converted into an electrode. This was accomplished using the fabrication procedure shown schematically in Figure 1. One face of the membrane was first sputter-coated with a thin (ca.  $50\text{ nm}$ ) layer of Au; this Au layer was too thin to bridge-over the pores at the Anopore surface (Figure 1b). Ag-Epoxy (Epotech 410-E) was used to attach a Cu lead wire to this Au film (Figure 1c).

The membrane/electrode was then immersed into a commercial Au plating solution (Orotep 24, Technics, Inc.). Au was galvanostatically electroplated on top of the sputter-coated Au layer (current density =  $2\text{ mA/cm}^2$ ). Electroplating was continued until the pores were completely covered with Au (5 min) (see Figure 1d). This thick electroplated Au layer was then covered

with epoxy (Torr Seal, Varian). Part of the opposite ( $\text{Al}_2\text{O}_3$ ) side of the membrane was also coated with epoxy so that only a  $0.5 \text{ cm}^2$  area of the Anopore membrane was left exposed (Figure 1e).

An Au microelectrode is present at the base of each of the pores in the exposed portion of the Anopore membrane shown in Figure 1e. These Au electrodes were used to electrochemically synthesize a polypyrrole fiber in each of the Anopore pores. An acetonitrile solution which was 0.5 M in pyrrole and 0.2 M in  $\text{Et}_4\text{NBF}_4$  was used for these polymerizations. A conventional one-compartment cell with a Pt counter and a saturated calomel reference electrode was employed. Polymerization was accomplished galvanostatically at a current density of  $0.6 \text{ mA/cm}^2$  of exposed membrane area.

The electrosynthesis described above yields a composite of the porous Anopore host membrane and the polypyrrole fibers (Figure 1f). The host membrane was dissolved away by immersing the composite into 0.2 M NaOH for 15 min. This yielded an ensemble of isolated polypyrrole fibers, connected at their bases to the substrate Au layer (Figure 1g). An electron micrograph of such an ensemble is shown in Figure 2.

Synthesis of conductive polymer fibers necessitates exposure of the polypyrrole to strong base (see above). Strong base has a pronounced, and deleterious, effect on polypyrrole electrochemistry [11]. The work of Inganäs et al. suggested that the effects of strong base can be reversed by subsequent exposure of the base treated polypyrrole to strong acid [12]. Therefore the final step of our procedure for the preparation of polypyrrole fibers was to immerse the fibers in a solution of 1 percent  $\text{HBF}_4$  to remove any base from the polymer. Finally, the fibers were rinsed with water, rinsed with acetonitrile, and transferred to a solution of 0.2 M  $\text{Et}_4\text{NBF}_4$  in acetonitrile

for electrochemical characterization.

Preparation of Conventional Polypyrrole Films. Conventional polypyrrole films were synthesized (as per above) onto  $0.5 \text{ cm}^2$  Pt disk electrodes [9]; a current density of  $1 \text{ mA/cm}^2$  was employed. To assess the effects of the base/acid treatment, discussed above, on the electrochemistry of polypyrrole, several of the conventional films were also treated with the base/acid regimen.

Electrochemical Analysis. A large amplitude potential step experiment was used to evaluate the rates of reduction of the various polypyrrole films. The film was first equilibrated at an applied potential of  $0.15 \text{ V vs. SCE}$ ; the film is quantitatively oxidized at this potential. The potential was then stepped to a final potential of  $-0.65 \text{ V vs. SCE}$  [13]; this drives the film reduction process to completion. The charge-time transient associated with reduction of the polymer film was recorded.

Because the reduction of the film is driven to completion, the charge-time transient ultimately reaches a plateau value (see e.g. Figure 3). The time required to achieve 95 percent of this plateau charge ( $t_{95}$ ) was used as the qualitative measure of the rate of the reduction process. Comparisons of  $t_{95}$  values between films will only be valid if the films contain the same total quantity of polypyrrole. The quantity of polypyrrole can be controlled by varying the charge delivered during the polymerization. We prepared various fibrillar and conventional films, containing the same quantity of polypyrrole, so that  $t_{95}$  values could be compared.

## RESULTS AND DISCUSSION

Figure 3 shows the charge time transients for an untreated conventional polypyrrole film, a conventional polypyrrole film which had been given the base/acid treatment (vida supra), and a fibrillar polypyrrole film (also



treated with base/acid). All of the films contain the same amount of polymer. Note first that all three films deliver the same total quantity of charge (plateau value is the same for all films). Thus, neither base/acid treatment nor changing to the fibrillar supermolecular structure changes the stoichiometry of the "doping" reaction.

Figure 3 also shows that the base/acid treatment diminishes the rate of charge-transport (compare the charge-time transients for the treated and untreated conventional films). In spite of the deleterious effect of the base/acid treatment, the rate of reduction for the fibrillar film is significantly higher than for the conventional films (Figure 3). This point is reinforced by the  $t_{95}$  data shown in Table I. For each quantity of polypyrrole, the fibrillar film shows significantly lower  $t_{95}$ 's than the conventional film. These data clearly indicate that the rate of reductive charge-transport is faster in the fibrillar films than in the conventional films.

#### CONCLUSIONS

We have shown that polypyrrole films with a fibrillar supermolecular structure support higher rates of reductive charge-transport than equivalent films with the conventional morphology. Since the reduction of polypyrrole corresponds to the discharge reaction in a polypyrrole battery, the data obtained here suggest that batteries incorporating fibrillar polypyrrole cathodes could deliver higher current densities than analogous batteries incorporating conventional polypyrrole cathodes. It is also worth noting that in addition to the higher charge-transport rates presented here, we have shown that extremely narrow conductive polymer fibers have much higher electronic conductivities than corresponding conventional polymer films [14].

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## References

1. *Handbook of Conducting Polymers*; Skotheim, T. A. E.; Marcel Dekker: New York, 1986.
2. A. F. Díaz and J. I. Castillo, *J. Chem. Soc. Chem. Comm.*, (1980) 397.
3. D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, 109 (1987) 3574.
4. L. L. Miller, B. Ainger and Q.-X. Zhou, *J. Am. Chem. Soc.*, 109 (1987) 3574.
5. D. Naegle and R. Bittihn, *Solid State Ionics*, 28-30 (1988) 983.
6. B. P. Kittlesen, H. S. White, and M. S. Wrighton, *J. Am. Chem. Soc.*, 106 (1984) 7384.
7. M. Gazard, in *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York 1986, Vol 1, Chapter 19.
8. R. M. Penner and C. R. Martin, *J. Electrochem. Soc.*, 133 (1986) 2206.
9. R. M. Penner, L. S. Van Dyke, and C. R. Martin, *J. Phys. Chem.*, 92 (1988) 5274.
10. Anopore is a trademark of Anotech Separations.
11. W. Wernet and G. Wegner, *Makromol. Chem.*, 188 (1987) 1465.
12. O. Inganäs, R. Erlandsson, C. Nylander and I. Lundström, *J. Phys. Chem. Solids*, 45 (1984) 427.
13. For the conventional polypyrrole films which were not treated with base/acid these potentials were shifted 50 mV positively. These potentials were selected to maintain the same overpotential (based on the position of the voltammetric waves) for all films.
14. Z. Cai and C. R. Martin, *J. Am. Chem. Soc.*, 111 (1989) 4138.

Table I.  $t_{95}$  values associated with the reduction of various polypyrrole films.

Polymerization Charge (mC)	$t_{95}$ (sec) <sup>a</sup>		
	Untreated	Treated <sup>b</sup>	Fibrillar <sup>b</sup>
	Conventional	Conventional	
95	$4.0 \pm 1.2$	$6.6 \pm 1.2$	$1.7 \pm 0.4$
190	$6.5 \pm 0.4$	$10.7 \pm 0.7$	$2.7 \pm 1.6$
285	$7.2 \pm 0.8$	$12.2 \pm 2.3$	$3.7 \pm 0.5$
380	$9.3 \pm 0.8$	$15.3 \pm 0.6$	$5.9 \pm 2.1$

<sup>a</sup> Time required to reduce the film to 95 % of maximum charge value.

<sup>b</sup> Polymer was exposed to base, then exposed to acid, see text.

### Figure Captions

Figure 1 Schematic of preparation of fibrillar polypyrrole. See text for details.

Figure 2 Scanning electron micrograph of fibrillar polypyrrole.

Figure 3 Charge vs. time transients for the reduction of various polypyrrole films. All films contained the same quantity of polypyrrole (polymerization charge = 190mC). — conventional polypyrrole film which had been treated with base then acid (see text for details). — untreated conventional film. — fibrillar film.

# Schematic of Fabrication Procedure For Preparing Fibers From Anopore Alumina Membranes

